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(54) IMPROVEMENTS IN AND RELATING TO HEAT-RECOVERABLE PRODUCTS

(71) We, RAYCHEM LIMITED, a British Company, of Cheney Manor, Swindon, Wiltshire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to heat-recoverable products and to compositions for preparing such products.

The materials to which the present invention relates are fluorinated elastomers obtained by polymerizing vinylidene fluoride with one or more fluorinated olefins. Examples of such fluorinated olefins are hexafluoropropylene, tetrafluoroethylene and 1-hydropentafluoropropene, and examples of the fluorinated elastomers used according to the invention are the Viton (Trade Mark) materials produced by E. I. Du Pont de Nemours. Thus, for example, Viton A is a copolymer of vinylidene fluoride and hexafluoropropylene, while Viton B is a terpolymer of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene. Polymers of the type described above have excellent resistance to heat, solvents, ozone and oxidation, and these properties, coupled with an inherent non-burning characteristic, make them outstanding among rubbers.

The normal processing sequence for a polymer of the type described above is typically as follows:—formulation; compounding; fabrication to the final shape; and crosslinking. Typical ingredients in addition to the polymer itself are, for example, magnesium oxide, carbon black, curing agents and lubricants according to the fabrication technique to be used and the performance required of the end product. In general the compounding and fabrication techniques are similar to those used for other elastomers. The crosslinking step may be carried out by chemical means, for example by the use of amines or peroxides, or by means of high energy radiation,

for example irradiation by gamma rays or accelerated electrons. In most cases, the crosslinking is followed by a post cure at elevated temperatures, for example, a post cure for a total of 24 hours at temperatures increasing from 140°C to 200°C.

Typical peroxide crosslinking agents which may be used for fluorinated elastomers are dicumyl peroxide and benzoyl peroxide, while suitable amine curing agents include hexamethylene diamine carbamate and N,N'-dicinnamylidene hexanediamine. Accelerated electrons may be produced, for example, by a van der Graaf generator or resonant transformer, and gamma rays may be produced by a suitable radio-active source, for example, a cobalt 60 source. The usual dose to produce a satisfactory degree of crosslinking is about 10 megarads.

One common application of fluorinated polymers of the type described above is in the shrouding of electrical wiring near the engines of jet aircraft. The construction of such a wiring harness is an expensive task as it involves a number of expensive operations, which may be outlined as follows:—

- 1) The preparation of a mould to accommodate the shape of the wiring harness required, which will include a number of junctions and cable terminations in connectors;
- 2) The lay-up of the appropriate wires within the mould;
- 3) Injection of the fluorinated polymer into the mould, followed by a cure cycle, which is then followed by the post-curing sequence.

Wiring harnesses made in this fashion suffer from three major faults. First, during the injection process the high pressures involved frequently cause a fracture of the wires in the harness. Secondly, it is extremely diffi-

cult to ensure that the wires are in the centre of the polymer jacket. Thirdly, if a modification to the shape of the harness is necessary a very expensive metal mould must be modified.

One of the major advantages of the heat-shrinkable products of the "Thermofit" system introduced some years ago is that it eliminates the need for expensive moulds in harness making by replacing them by a wide range of different shapes of moulded parts and a large number of different sized tubings all of which shrink to a predetermined extent on the application of heat. "Thermofit" is a Trade Mark. By the use of these moulded parts and tubings, the most complicated harnesses can be made without the use of expensive moulds or moulding equipment or the need for highly experienced labour.

As the fluorinated polymers of the type described above are elastomers it would seem unlikely that heat-shrinkable products could be made from them without some modification. The reason for this is that most heat-shrinkable materials rely on a change of crystallinity somewhere above their storage temperature. Polyethylene, for example, which is partially crystalline at room temperature and amorphous at a temperature of about 130°C, can be crosslinked, for example, by irradiation, to produce a material which has strength above its crystalline melting point and which at that temperature behaves like rubber. Such cross-linked polyethylene can be converted to a state in which it is heat-shrinkable, that is to say, when heated to a temperature above its crystalline melting point, deformed from its original shape and cooled in its deformed state to a temperature below its crystalline melting point, it retains the deformed shape. If it is then again heated to a temperature above its crystalline melting point it will recover the original shape that it had prior to deformation. Attempts have been made to render Viton heat-shrinkable by incorporating in it a homopolymer of vinylidene fluoride (a partially crystalline material), but the material obtained is less flexible than Viton and partially loses many of its rubbery characteristics. In addition, the heat-ageing characteristics of the blend may well be less good than those of the Viton.

The present invention is based on the observation that heat-shrinkable properties can be imparted, without the addition of a crystalline additive, to a crosslinked fluorinated polymer of the type described above.

The present invention provides an article comprising a crosslinked fluorinated polymer, the fluorinated polymer being a copolymer of vinylidene fluoride and one or more fluorinated olefins, to which the property of elastic memory (sometimes referred to as plastic memory) has been imparted by heating it to

a temperature at which it can be deformed, subjecting it to a deforming force at that temperature and cooling it while it is maintained in the deformed state to a temperature at which the deformed state is maintained when the deforming force is removed. The fluorinated olefin(s) is or are advantageously selected from hexafluoropropylene, tetrafluoroethylene and 1-hydropentafluoropropene. The copolymer may be, for example, a copolymer of vinylidene fluoride and hexafluoropropylene, or a terpolymer of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene.

The present invention also provides a process for the manufacture of an article as defined above, wherein a fluorinated polymer of the type described above is formed to a desired shape, crosslinked, heated to a temperature at which it can be deformed, subjected to a deforming force at that temperature and cooled while it is maintained in the deformed state to a temperature at which the deformed state is maintained when the deforming force is removed. The article is preferably deformed at a temperature in the range of from 150° to 200°C.

The cooling of the article to a temperature below that at which the article is deformed may be carried out by cooling it, for example, to room temperature and maintaining it at that temperature for a period of from, for example, 3 hours to 3 days. Preferably, however, the article is cooled to a temperature below room temperature for a short time, for example by cooling to -60°C for 3 hours, since it has been suggested that its shrinkage ratio can be increased in this way.

The crosslinking of the copolymers used in the articles of the present invention may be effected by chemical means, for example, using a free radical polymerization initiator, or by other means, for example, by high energy irradiation. The crosslinking is continued until at least a part of the polymer is crosslinked.

The articles of the present invention which "remember" the shape they had before deformation when they are reheated to the temperature at which they were deformed without the influence of the deforming force, can be made from the crosslinked copolymers by forming the copolymer to a desired shape article and imparting the property of elastic memory as specified above.

The elastic memory articles, which may be in the form of tubings or other moulded parts are admirably suited for the production of harness moulds for electrical wiring near the engines of jet aircraft.

In making the articles of the present invention other ingredients, for example, fillers may be incorporated in the fluorinated polymer. Thus it is possible to mill in ingredients such, for example, as magnesium oxide, carbon black, curing agents or antioxidants, as desired, on a two-roll mill set at approximately

50°C. Processing may then be continued as outlined above.

The following Examples illustrate the invention.

- 5 For Examples 1 and 2 the following formulation was used:

	parts by weight
Viton AHV	100
Carbon black (Thermax)	25
10 Magnesium Oxide	5
Dibasic Lead fumarate	5
Triallyl Cyanurate	2
2,5 - dimethyl - 2,5 - di -	
(tertiary butyl peroxy) -	
15 hex - 3 - yne	1

Viton AHV is a copolymer of vinylidene fluoride and hexafluoropropylene. "Thermax" is a Trade Mark.

- 20 The ingredients were cold milled together on a two-roll mill and from the resulting composition cylinders were hot moulded which were 3 inches long, 0.6 inch in diameter with a wall thickness of 0.125 inch. The cure conditions were 12 minutes at 200°C.

EXAMPLE 1

- Rings 0.25 inch wide cut from the cylinders obtained as described above were expanded on a polytetrafluoroethylene mandrel at 200°C to a ratio of 4:1, cooled while on the mandrel to room temperature for 15 minutes, and then removed. 3 days later the expansion ratio was 2:1 and 7 days later this was unchanged. When the samples were again heated to 200°C to bring about recovery the rings returned to their moulded diameter. This example illustrates that a shrinkage ratio of 2:1 can be achieved, and that the amount of strain retained by the material capable of being recovered subsequently is $\frac{1}{3}$ of that applied.

EXAMPLE 2

- Further rings of the type described above were expanded to a ratio of 3:1, cooled, while on the mandrel, at room temperature for 15 minutes and then removed. 3 days later the residual expansion ratio was 1.7:1 and 7 days later this was unchanged. When the samples were again reheated to 200°C to bring about recovery, the rings returned to their original moulded diameter thus showing a shrinkage ratio of 1.7:1; in this instance the amount of strain retained by the material was 0.35 of that applied.

- For examples 3 and 4 the formulation used was as follows:—

	parts by weight
Viton AHV	100
Carbon black (Thermax)	25
Magnesium Oxide	15
Triallyl Cyanurate	2
2,5 - dimethyl - 2,5 - di -	
(tertiary butyl peroxy) -	
hex - 3 - yne	2

Using the moulding technique and curing conditions outlined in Examples 1 and 2 further samples of rings were obtained.

EXAMPLE 3

The samples were expanded at 200°C, cooled on the expansion mandrel (which was three times the original internal diameter of the sleeve) for 15 minutes at room temperature and the mandrel was then removed. The sample was stored at room temperature for a further 30 minutes and then remeasured. In this instance the shrinkage ratio remaining was 1.45:1.

EXAMPLE 4

Further samples were expanded as described above, but instead of being cooled at room temperature were cooled on the mandrel for 15 minutes at -60°C, then removed and stored at room temperature for 3 hours. After this time the shrinkage ratio remaining was 1.52:1.

The comparison between Examples 3 and 4 illustrates the fact that quenching at a low temperature in the expanded form enables the material to retain a higher shrinkage ratio subsequently.

EXAMPLE 5

A formulation comprising:—

	parts by weight
Viton B	100
Carbon black (Thermax)	25
Magnesium Oxide	15
Triallyl Cyanurate	2
2,5 - dimethyl - 2,5 - di -	
(tertiary butyl peroxy) -	
hex - 3 - yne	2

Viton B is a terpolymer of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene.

The ingredients were cold milled on a two roll mill and from the resulting compound cylinders were moulded 5 inches in length, 0.5 inch in internal diameter and 0.10 inch in wall thickness using a transfer moulding technique. The cure time was 10 minutes at

200°C in addition to a transfer time of 3 minutes.

- 5 Rings 0.25 inch wide were cut from these cylinders and these were expanded in a ratio of 4:1 as described in Example 1. After conditioning for 3 days at room temperature the retained shrinkage ratio was 1.7:1 and a further 7 days conditioning did not further reduce this figure.

- 10 Subsequently on reheating to 200°C the rings returned to their original internal diameter of 0.5 inch.

EXAMPLE 6

- 15 The two mixes given below were compounded on a cold two roll mill to form hides which were then pressed into uniform plaques, and cured for times given.

- 20 Dumbbells were cut from these plaques, marked with a one inch gauge, then extended, at 200°C. The dumbbells were then cooled in the extended state and the gauge length measured; after a further 75 hours at room

temperature the gauge length was remeasured. The dumbbells were then shrunk down using a temperature of 200°C, and the recovered gauge length determined. The table shows the results of this experiment.

Mix	1	2	
Viton AHV	100	100	
Magnesium Oxide	15	15	30
Thermax	25	25	
Copper Inhibitor	2	—	
Diak No. 3	2	—	
Hercules Peroxide S 890	—	2	
Triallyl Cyanurate	—	—	35

Diak No. 3 is N,N' - dicinnamylidene - 1,6-hexane diamine and the active ingredient of the copper inhibitor is disalicylal propylene diamine.

Cure			
Temperature	150°C	150°C	40
Time	60 mins.	60 mins.	

TABLE

Gauge length measurements

Mix	Original Length (inches)	Length when Stretched (inches)	Length after 75 hrs. at 20°C. (inches)	Recovered Length (inches)
1	1.0	2.85	2.0	1.02
2	1.0	2.0	1.5	1.02

WHAT WE CLAIM IS:—

- 45 1. An article comprising a crosslinked fluorinated polymer, the fluorinated polymer being a copolymer of vinylidene fluoride and one or more fluorinated olefins, to which the property of elastic memory has been imparted by heating it to a temperature at which it can be deformed, subjecting it to a deforming force at that temperature and cooling it while it is maintained in the deformed state to a temperature at which the deformed state is maintained when the deforming force is removed.

- 50 2. An article as claimed in claim 1, wherein the fluorinated olefin(s) is or are selected from hexafluoropropylene, tetrafluoroethylene and 1-hydropentafluoropropene.

- 60 3. An article as claimed in claim 1 or claim 2, wherein the fluorinated polymer is a copolymer of vinylidene fluoride and hexafluoropropylene.

4. An article as claimed in any one of claims 1 to 3, which also comprises one or more further ingredients selected from fillers, curing agents and antioxidants.

5. An article as claimed in any one of claims 1 to 4, which is so shaped as to be capable of providing a wiring harness.

6. An article as claimed in any one of claims 1 to 4, which is in the form of a tube.

7. An article as claimed in any one of claims 1 to 6, which has been crosslinked by chemical means.

8. An article as claimed in any one of claims 1 to 6, which has been crosslinked by high energy irradiation.

9. An article as claimed in claim 1 and described in any one of the Examples herein.

10. A process for the manufacture of an article as claimed in claim 1, wherein a copolymer of vinylidene fluoride and one or more fluorinated olefins is formed to a desired shape,

- crosslinked, heated to a temperature at which it can be deformed, subjected to a deforming force at that temperature and cooled while it is maintained in the deformed state to a temperature at which the deformed state is maintained when the deforming force is removed. 5
11. A process as claimed in claim 10, wherein the article is deformed at a temperature in the range of from 150° to 200°C.
- 10 12. A process as claimed in claim 10 or claim 11, wherein the deformed article is cooled to room temperature and maintained at that temperature for a period of from 3 hours to 3 days before the deforming force is removed. 15
13. A process as claimed in any one of claims 10 to 12, wherein the article is cross-linked by chemical means.
14. A process as claimed in any one of claims 10 to 12, wherein the article is cross-linked by high energy irradiation. 20
15. A process as claimed in claim 10 carried out substantially as described in any one of the Examples herein.
16. A method of providing a substrate with a covering, which comprises positioning an article as claimed in claim 5 or claim 6 around the substrate, the article being heat-shrinkable, and heating the article at least to the temperature at which it was deformed to cause it to shrink tightly around the substrate. 25 30
17. An assembly whenever produced by a method as claimed in claim 16.
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